DEVELOPMENT AND VALIDATION OF A REDUCED MF/BIODIESEL MECHANISM FOR DIESEL ENGINE APPLICATION

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2-methylfuran (MF) is widely used as a surrogate fuel for internal combustion engines. However, the chemical kinetics model of MF for engine combustion simulations remains scarce. In this paper, a reduced MF/biodiesel mechanism consisting of 82 species and 226 reactions was proposed and used to simulate the combustion process of MF and biodiesel dual-fuel diesel engine. First, a detailed chemical reaction mechanism of MF was selected and then mechanism reduction methods were used to reduce the detailed mechanism under engine conditions. Second, the reduced MF mechanism was coupled with a biodiesel mechanism to form a four-component chemistry mechanism, consisting of MD, MD9D, n-heptane and MF. Third, the combined mechanism was optimized by using rate of production analysis and sensitivity analysis. Finally, the proposed four-component mechanism was verified by comparing the calculated values of ignition delay and species concentrations with the experimental values. Meanwhile, a new dual-fuel diesel engine test was carried out, and the experiments were used to evaluate the reliability of the combination mechanism. Overall, the simulated results of the proposed four-component mechanism in this paper are basically consistent with the experimental results.

Keywords: 2-methylfuran; biodiesel; reaction mechanism; dual-fuel engine

1. Introduction

Since the 21st century, in order to overcome the scarcity of fossil fuels, researchers have to find clean renewable fuels which can replace traditional fossil fuels. Among various surrogate fuels, biodiesel and alcohols have aroused great interest as substitutes for automobile fuel. Biodiesel is a monoalkyl ester of long-chain fatty acids extracted from animal fats or vegetable oils [1], which has the key properties of non-toxic, high cetane number, high oxygen content, non-sulfur, high inherent lubricity and biodegradability. These properties make this fuel an ideal substitute for fossil diesel. Alcohols are regarded as substitutes for gasoline or additives for diesel. Ethanol is the most widely studied, but its application is limited because of its low energy density, high production cost, strong volatility and high water solubility [2,3]. Therefore, many studies have been carried out to find better gasoline substitutes or diesel additives than alcohols.

With the in-depth research on biofuels, 2-methylfuran (MF) has attracted more and more attention as a promising renewable fuel for internal combustion engines. MF can be produced from non-edible biomass [4-6] and the potential of MF as surrogate fuel on engine has been proved [7,8]. As shown in Table 1 [9-11], the boiling point of MF is similar with gasoline, and its high octane number makes it suitable as a substitute for gasoline. In addition, MF has several advantages over smaller alcohols. MF has higher energy density (~29 MJ/L) compared to ethanol (~21 MJ/L) and n-butanol (~27 MJ/L), which is close to gasoline (~32 MJ/L) [12].
The applicability of MF fuel as gasoline surrogate fuel or diesel additives in internal combustion engines has been experimentally evaluated in many studies. Wang et al. [7] investigated the performance of a direct-injection spark-ignition (DISI) engine fueled with MF, ethanol, gasoline and 2,5-dimethylfuran (DMF). The experiments showed that MF produces a higher indicated thermal efficiency than gasoline and DMF, and the emissions of aldehydes of MF are lower than those of gasoline and ethanol. Feng et al. [13] studied the combustion and emissions performance of MF/gasoline mixtures on a spark-ignition (SI) engine. The results showed that compared with gasoline, MF has better knock suppression ability. Meanwhile, the combustion duration of MF/gasoline mixtures was shorter, and the maximum in-cylinder pressure and average temperature were higher than those of gasoline. And the emissions of hydrocarbon (HC) and carbon monoxide (CO) were significantly reduced. Sivasubramanian et al. [14] conducted an experimental study on the effects of MF addition on engine combustion performance and emissions performance in a four-stroke multi-point fuel injection (MPFI) SI engine. The experimental results showed that with the increase of blend percentage, the ignition delay time was reduced, the emissions of CO and HC decrease, while braking thermal efficiency (BTE) and nitrogen oxides (NOx) emissions increase. Xiao et al. [15-17] studied the performance of MF/diesel and MF/biodiesel blends in a direct-injection compression-ignition (DICI) engine. They found that MF/diesel mixtures have longer ignition delays, shorter combustion duration and higher BTE. Meanwhile, MF addition could effectively reduce the emissions of HC, CO and soot, while the emissions of NOX are increased. Liu at al. [18] investigated the performance of MF in a DISI engine and found that when considering combustion phasing and knock limit, the spark timing range of MF is larger than that of gasoline. Compared with gasoline and ethanol, MF has more robustness to lean combustion.

The chemical kinetics mechanism of MF has also been studied by several researchers. Somers et al. [19] proposed a detailed DMF mechanism with 545 species and 2768 reactions, which includes the chemistry mechanism of MF. The prediction ability of detailed mechanism was widely evaluated by comparing with the experimental measurements, including ignition delays at pressure of 1, 20 and 80 bar, equivalence ratios (ERs) of 0.5-2.0 and temperature of 820-1800 K, jet-stirred reactor (JSR) species mole fraction profiles at temperatures of 770-1220 K, 10.0 atm, and ERs of 0.5-2.0, and laminar burning velocities at atmospheric pressure, temperatures of gas at 298 and 358 K and ERs of 0.6-1.6. Later, Somers et al. [20] modified the reaction rates of MF by statistical rate theory, quantum chemical calculation and chemical kinetic model. Somers et al. [21] also proposed a chemical kinetic model for MF oxidation consisting of 391 species and 2059 reactions. The ignition delays predicted by this mechanism were evaluated by experimental results of shock tube ignition delays at pressure of 1 atm, temperatures of 1200-1800 K and ERs of 0.5-2.0, and laminar flame velocities at temperatures from 298 to 398 K, pressure of 1 atm and ERs of 0.55-1.65. They found that the developed mechanism could accurately predict the experimental measurements. Tran et al. [12]
developed a detailed chemical kinetic model for MF oxidation, which is composed of 305 species and 1472 reactions. It was verified by comparing the predicted species mole profiles with the experimental data in MF/O\textsubscript{2}/Ar at pressures of 20 and 40 mbar and ERs of 1.0 and 1.7.

From the works above, the reduced MF/biodiesel mechanism applicable to diesel engine simulation has not been reported. This paper presents a reduced four components mechanism, consisting of MF, MD, MD9D and n-heptane, for simulate MF/biodiesel dual-fuel engine. And the performance of this mechanism was verified by comparing the simulations and the experimental measurements of ignition delays in shock tubes and species mole fractions in laminar premixed flames. In addition, the combustion performances of biodiesel and MF was studied on a dual-fuel diesel engine, and the reduced mechanism was further evaluated by comparing with the experimental results.

2. Kinetic model construction

2.1. Base biodiesel mechanism

The biodiesel mechanism with 69 species and 192 reactions developed by Brakora et al. \cite{22} was adopted as base mechanism, in which a mixture of 25\% methyl decanoate (MD), 25\% methyl-9-decanoate (MD9D) and 50\% n-heptane were used as biodiesel surrogate fuels, where MD and MD9D were respectively used as the surrogates for saturated and unsaturated species in actual biodiesel, and n-heptane was used to improve ignition behavior. Then they investigated experiments to prove the accuracy of the mechanism. And the results showed that, at low speed, high load, the performance and NOx formation of the experiment are accurately predicted by the mechanism and the kinetic model can also well-predicted the consumption of HC, CO, NOx and fuel at high speed and low load.

2.2. The reduced MF mechanism

A detailed mechanism of MF oxidation proposed by Tran et al. \cite{12}, consisting of 305 species and 1472 reactions, was selected as the initial mechanism. First, the direct relation graph error propagation (DRGEP) method was employed to systematically remove the decoupled species and unrelated reactions at a chosen error limit of 30\% in the first reduction process. The reduction process of the detailed MF mechanism was carried out at the pressure of 1-10 atm, temperature of 800-1600 K within the ERs of 0.5-2.0. In each reduction step, the performance of the ignition delay of generated reduction mechanism is compared with the startup mechanism to ensure that it maintains an acceptable predictive ability. Second, manual reductions were carried out by using the methods of rate of production analysis (ROPA) and sensitivity analysis (SA). Third, isomer lumping method was used to further reduce the number of reactions. Finally, a reduced MF mechanism consisting of 42 species and 148 reactions was formed.

A reaction path analysis of the reduced MF mechanism and simulation time corresponding to around 20\% fuel conversion was conducted in a homogeneous batch reactor for an ignition process of stoichiometric MF/O\textsubscript{2}/Ar mixtures at 40 bar pressure and 1300 K. As shown in Fig. 1, there are two major consumption paths of MF. MF is primarily consumed (~70.2\%) by H-abstractions from the methyl group forming the furylCH\textsubscript{2} radical. Then about 63.8\% furylCH\textsubscript{2} radicals were isomerized to form OCHCHCHCCH\textsubscript{2} radical, and then OCCHCHCHCH\textsubscript{2} radical were formed. OCCHCHCHCH\textsubscript{2} decomposed into the C\textsubscript{2}H\textsubscript{5} radical and CO by $\alpha$-cleavage of the C-C bond and about 36.2 \% furylCH\textsubscript{2} yields furylCH\textsubscript{2}O and then generates furyl-2. A second important path of consumption of MF is to yield furan by ipso-addition. As for the decomposition of furan, about 68.9\% of furan yields C\textsubscript{2}H\textsubscript{2}CHO by OH-addition at the C=C double bond and further cleavage to C\textsubscript{2}H\textsubscript{2}. About 31.1 \% of furan generates furyl-2 by H-abstractions at C2 position. furyl-2 further cleavage to CH\textsubscript{2}CHCO and CHCHCO.
Fig. 1 Reaction path analysis carried out at 20% fuel consumption under shock tube conditions at T=1300K, 40bar for stoichiometric MF/nitrogen/O\textsubscript{2} mixtures.

2.3. The combined mechanism

The reduced MF mechanism is coupled with Brakora biodiesel mechanism [22], and the repetitive reactions in the base mechanism were remained. After the merger process, a combined mechanism with 82 species and 226 reactions was obtained. Initial shock tubes simulation results showed that the calculated value of the ignition delay by this combined mechanism has a large error with the experimental value, so it is necessary to optimize the combined mechanism.

Based on the ROPA and SA methods, several reactions were adjusted in this base mechanism to improve its prediction of ignition delays. The following reaction (R1) is most sensitive to the ignition delays of n-heptane and the pre-exponential factor was adjusted from 1.355E+10 to 1.355E+13. The reaction with high sensitivity to MD9D ignition delay is (R2), and the pre-exponential factor of (R2) was adjusted from 2.5E+10 to 2.5E+8.

\[
\text{NC}_7\text{H}_{16}+\text{OH}=\text{C}_7\text{H}_{15}-2+\text{H}_2\text{O} \quad \text{(R1)}
\]

\[
\text{MF}_5\text{O}_2=\text{MF}_5\text{OOH}_2 \quad \text{(R2)}
\]

In addition, it was found that the two reactions of (R3) and (R4) are the most sensitive to MF ignition delay times in the combined mechanism. Thus the reaction rate coefficients of (R3) was adjusted from 1.0E+14 to 1.0E+13 in this study, while (R4) was adjusted from 4.5E+16 to 4.5E+18 to match the experimental ignition delays.

\[
\text{C}_4\text{H}_5=\text{C}_2\text{H}_2+\text{C}_2\text{H}_3 \quad \text{(R3)}
\]

\[
\text{C}_2\text{H}_4+\text{O}_2=\text{HCO}+\text{C}_2\text{H}_3\text{CHO} \quad \text{(R4)}
\]

Finally, a reduced MD/MD9D/n-heptane/MF mechanism which contains 82 species and 226 reactions was formed.

3. Mechanism validation

Ignition delays, premixed flame species mole fraction, dual-engine in-cylinder pressure predicted by the proposed MD/MD9D/n-heptane/MF mechanism were compared and verified with the measurement results in this section.

3.1. Ignition delay times
Fig. 2 shows the comparison of the predicted ignition delays of n-heptane of the reduced mechanism with measurements of Ciezki et al. [23] and Hartmann et al. [24] under the ERs of 1.0 and 2.0, and initial pressures of 13.5–42 bar. As shown in Fig. 2, the proposed mechanism can well-predict the experimental shock tube data of n-heptane, especially the negative temperature coefficient (NTC) phenomenon could be well captured.

![Fig. 2](image1.png)

**Fig. 2** Measured [23,24] (symbols) and predicted (lines) ignition delays of n-heptane

Wang et al [25,26] studied the experiment of the ignition delays of MD/air blends at pressures of 16 and 21 bar, temperatures of 650–1350K within the ERs of 0.5, 1.0, and 1.5. Fig. 3 shows the comparison between ignition delays predictions and the experimental data of MD. It could be seen that the reduced mechanism can accurately predict the ignition delays of MD. and decrease of the ignition delays with increase of ERs could be well captured, indicating that the reduced mechanism can ensure the accuracy of the prediction of MD ignition delays data.

![Fig. 3](image2.png)

**Fig. 3** Measured [25,26] (symbols) and predicted (lines) ignition delays of MD

Ignition delays of MD9D/air mixtures under the pressure of 20 bar within the temperature from 650 to 1350 K and ERs of 0.5–1.5 were measured by Wang et al. [26]. In Fig. 4, the predicted ignition delays by reduced mechanism was compared with the experimental data. It can be seen that the reduced mechanism satisfactorily predict the measurements, and the phenomenon that ignition delay times are decreased with the increase of ERs was observed. In general, the proposed mechanism can reasonably sufficient to simulate the ignition delays of MD9D.

Fig. 5 compares of the ignition delays of stoichiometric MF simulated by the proposed mechanism with the experimental data of Eldeeb et al. [27] at the pressures of 2, 5, and 10 atm within the temperature range
from 977 to 1570 K. As seen, the ignition delays increase with the decrease of pressure could be reasonably captured by the reduced mechanism under studied temperature range, which indicates the reduced mechanism can accurately reproduce the measurements under different initial pressure.

![Graph](image1)

**Fig. 4** Measured [26] (symbols) and predicted (lines) ignition delays of MD9D

![Graph](image2)

**Fig. 5** Measured [27] (symbols) and predicted (lines) ignition delays of MF

### 3.2. Premixed flame species profiles

Seidel et al. [28] experimentally investigated premixed stoichiometric flame of n-heptane/oxygen/argon mixtures at pressure of 0.04 bar. Fig. 6 compared the species mole fraction profiles of experimental values and the predicted values of the reduced mechanism in n-heptane premixed flame. For comparison, the simulated results of Brakora mechanism [22] were also included.

As shown in Fig. 6(a)-(c), the reduced mechanism accurately predicts the experimental measurements of the concentrations of n-heptane, O$_2$, Ar and CO, but there are some discrepancies in CO$_2$, H$_2$O and H$_2$ concentrations. At the lower height of above burner (HAB), the simulations of H$_2$ and CO$_2$ are lower than the experimental measurements, while the simulation of H$_2$O are higher than the measurements. With the consumption of n-heptane, the simulated concentration values of CO$_2$, H$_2$O and H$_2$ are gradually close to the experimental data. In addition, although the reduced mechanism can accurately predict the concentration of major species, but the difference between simulations and experiments of intermediates is obvious, as shown in Fig. 6(e)-(g). Indeed, although the simulated intermediates by the proposed mechanism is different from the measurements, but the profile shapes of the simulated intermediate species are consistent with the experimental measurements. It is worth noting that the experimental measurements of H$_2$O, CO$_2$ and intermediates are also not well simulated by the Brakora mechanism [22].
Fig. 7 compares the experimental measurements [29] and predicted data of species mole fraction profiles in stoichiometric premixed MD flame at atmospheric pressure. Also, the simulation results of Brakora mechanism [22] were included. As shown in Fig. 7(a) and (b), the reduced mechanism accurately predict the concentrations of MD, O2 and H2O, but there are error in the concentrations of CO and CO2. The concentration of CO is higher than the experimental results at the lower HAB, while the simulation of CO2 is lower than the experimental results. Then with the consumption of O2 and MD, the simulations of CO2 and CO are gradually close to the experimental results. As for the mole fraction of intermediates, Fig. 7(c) showed that the simulations of intermediates are close to the measurements. Especially, the simulated species concentrations of C2H2 by the reduced mechanism are in excellent agreement with measurements.

Fig. 6 Measured [28] (symbols) and predicted (lines) species profiles in premixed n-heptane flame. Solid lines: the proposed mechanism, dashed lines: the Brakora mechanism [22]

Fig. 7 Measured [29] (symbols) and predicted (lines) species profiles in premixed MD flame. Solid lines: the proposed mechanism, dashed lines: the Brakora mechanism [22]

Fig. 8 compares the simulations of species mole fraction profiles in stoichiometric MD9D/air mixtures premixed flame at atmospheric pressure between the proposed mechanism and Brakora mechanism [22]. It
was observed that the calculated values of the two mechanisms are in reasonable agreement, indicating that the calculated ability of the MD9D sub-mechanism in Brakora mechanism [22] has been well preserved.

![Graphs showing species profiles](image1)

Fig. 8 the predicted species profiles of proposed mechanism (lines) and Brakora mechanism [22] (symbols) in premixed MD9D flame.

Tran et al. [12] studied the premixed MF flames for ERs of 1.0 and 1.7 at pressures of 0.02 and 0.04 bar. Fig. 9 compares the measurements and simulations of major species mole fraction in premixed MF flames. Also, the simulations of Tran mechanism [12] are included. It is observed from Fig. 9, the simulated results of MF, O₂, Ar and H₂ in premixed stoichiometric flame are consistent with experimental data, but some error between the simulations and experimental data for H₂O, CO₂ and CO has been found. As seen, the simulations of H₂O and CO₂ are lower than the experimental results and the simulation of CO is higher than the experimental data. In fuel-rich flame, the simulations of MF, O₂, Ar, H₂, CO are consistent with experimental results, but the simulations of H₂O and CO₂ are lower than the measurements. It is worth noting that the simulated results of H₂O and CO₂ of Tran mechanism [12] are also lower than the measurements.

![Graphs showing mole fraction vs. HAB](image2)
Fig. 9 Measured [12] (symbols) and predicted (lines) species profiles in premixed MF flames. Solid lines: the proposed mechanism, dashed lines: the Tran mechanism [12].

3.3. Dual-fuel engine combustion validation

To further validate the proposed reduced mechanism of MF/biodiesel, a new dual-fuel diesel engine experiment was conducted in a single-cylinder four-stroke diesel engine. A detailed description of experimental setup can be found in [30,31]. Fig. 10 depicts the schematic diagram of the experimental device. Engine specifications and experimental conditions could be found in Table 2 and Table 3. During the experiments, biodiesel was fed into cylinder by a common-rail high-pressure DI injector, and injection timing was set at -20 ° crank angle (CA) after the top dead center (ATDC). MF fuel was fed into intake port by a low-pressure injector which was installed at intake port, and injection timing was set at -300 °CA ATDC. Keeping the total energy of fuel supplied to engine for each cycle as constant (620.25J), under the RCCI combustion mode, the premixed ratios of MF/biodiesel dual-fuel was applied as 0%, 40% and 60% (referred to as D0, D40 and D60) over the energy amount. The multi-dimensional engine simulation was carried out by using the CONVERGE CFD code [32], and the proposed mechanism was imported into the ‘reaction mechanism’ module of CONVERGE as input file. Table 4 shows the physical models selections in the simulation. Fig. 11 shows the geometry of the test engine, and simulation range was from -155 °CA ATDC to 155 °CA ATDC.

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<th>Table 2 Engine specifications.</th>
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<td>DI fuel injector</td>
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<td>Port fuel injector</td>
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<th>Table 3 Engine operating conditions.</th>
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<td>Parameter</td>
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<td>EGR ratio</td>
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As shown in Fig. 12 showed the simulated value of in-cylinder pressure by proposed mechanism was compared with the experimental measurements. The simulations of in-cylinder pressure are in good agreement with the experiments in three simulated conditions, but there are error in the peak of in-cylinder pressure. As shown in Fig. 12(a) and (b), the simulations of reduced mechanism of combustion duration is longer than the experiments. The slight discrepancies between simulations and experiments may be due to there was no reasonable consideration on the effect of turbulence on chemical kinetics in the prediction. In addition, there may be some errors of the fuel injection rules between the simulation and experiments. In
general, the reduced mechanism could be used to predict the combustion process of MF/biodiesel dual-fuel engine.

![Graphs showing in-cylinder pressure comparisons](image)

**Fig. 12** Comparisons between the predicted (lines) and experimental (symbols) in-cylinder pressures.

### 4. Conclusions

In this work, a reduced MF/biodiesel dual-fuel mechanism with 82 species and 226 reactions was proposed for diesel engine applications. Firstly, the detailed MF mechanism of Tran et al. [12] was selected as the initial mechanism and then the mechanism was reduced by using DRGEP method. Subsequently, ROPA, SA and isomer lumping methods were used to further lessen the number of reactions of the obtained reduced MF mechanism, and a reduced MF mechanism composed of 42 species and 148 reactions was formed. Then the reduced MF mechanism was coupled with the biodiesel mechanism of Brakora et al. [22] to form a four-component (MF/MD/MD9D/n-heptane) reaction mechanism. Finally, a MF/biodiesel dual-fuel mechanism with 82 species and 226 reactions was obtained by optimizing the reaction rate coefficients in selected reactions. After that, simulations of the new reduced dual-fuel mechanism were compared with the existing experimental measurements, and the results showed that the reduced mechanism can give a good prediction.
of ignition delays and premixed flame species concentration. In addition, dual-fuel diesel engine experiments were carried out, and the reduced mechanism was evaluated using corresponding data. It was proven that the proposed mechanism can reasonably capture the experimental in-cylinder pressure. In conclusion, this new MF/biodiesel mechanism could be used to calculate the combustion characteristics of engine fueled with MF and biodiesel.

Acknowledgments

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Abbreviations

MF 2-methylfuran  
DMF 2,5-dimethylfuran  
HC hydrocarbon  
MPFI multi-point fuel injection  
NOx nitrogen oxides  
ERs equivalence ratios  
MD methyl decanoate  
DRGEP direct relation graph error propagation  
SA sensitivity analysis  
HAB height of above burner  
ATDC after the top dead center  
CFD computational fluid dynamics

DISI direct-injection spark-ignition  
SI spark-ignition  
CO carbon monoxide  
BTE braking thermal efficiency  
DICI direct-injection compression-ignition  
JSR jet-stirred reactor  
MD9D methyl-9-decanoate  
ROPA rate of production analysis  
NTC negative temperature coefficient  
CA crank angle  
RCCI reactivity Charge Compression Ignition

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